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A kinetic study of the base catalyzed esterification of propionic anhydride with isopropyl and n-propyl alcohols using a high frequency oscillometer

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A KINETIC STUDY OF THE BASE CATALYZED ESTERIFICATION OF PROPIONIC ANHYDRIDE WITH ISOPROPYL AND n-PROPYL ALCOHOLS USING A HIGH FREQUENCY OSCILLOMETER

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by

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CHAPTER I

INTRODUCTION

The purpose of this research project is to investigate the base catalyzed reaction of propionic anhydride with n-propyl and isopropyl alcohols using a high frequency (120 megacycles) oscillometer to follow the course of the reaction as it proceeds.

The high frequency oscillometer has been used for many types of analytical determinations, and a review of the work up to 1957 is available in a publication by E. H. Sargent Company. The oscillometer has found application in titrations (Hall 1952), analysis of binary systems (Thomas, Faegin, and Wilson 1951), static ternary systems (West, Robickaus, and Burkhalter 1951), the study of complexes (Hara 1952), and in the field of chromotography (Baumann and Blaedel 1956; Honda 1953, 1954).

When conductance or dielectric constant changes during the course of a reaction, reaction rates can be studied. Since no electrodes are present, the possibility of electrode contamination, polarization, and an electrical influence on the reaction as it progresses is eliminated. Crystallization velocity and precipitation velocity studies have been made (Asada 1954; Duke, Bever, and Diehl 1949), a saponification reaction has been followed (Jensen, Watson,

and Beekham 1951), and rates for the hydrolysis of lower aliphatic esters and esters of chloracetic acid have been measured (Elving 1954; Flom and Elving 1953).

The published kinetic studies using this type instrument have been done in aqueous solution. The principle instrumental effect in these studies is conductometric, whereas the utilization of the binary solution method of analysis in this project is essentially capacitative in its instrumental effect.

A study of the base-catalyzed solvolysis of acetic anhydride in methanol-water mixtures has been made (Koskikallis 1959) using a method involving consecutive titrations. The rate of this reaction is too fast to be studied using this instrument; however, to date, kinetic studies have been made on the base catalyzed esterification of acetic anhydride with ethyl alcohol (Lowery 1958) and isobutyl alcohol (Lewis 1959) using the high frequency oscillometer.

CHAPTER II

A DESCRIPTION OF THE INSTRUMENT

The instrument, as described in literature (Clinkscales and Frye 1960), is of the heterodyne type. It is composed of two separate oscillators, a working oscillator and a reference oscillator. The frequency of the working oscillator is determined by the components in the reacting vessel. Controlling the reference oscillator are two condensers in parallel which results in a large tuning range and allows one to find the frequency of the working oscillator easily. A heterodyne is detectable with the use of an earphone or oscilliscope as the oscillators approach the same frequency. When the two oscillators are of the same frequency, a zero beat is detected.

The change in electrical characteristics of a sample, which is a result of chemical composition, can be read directly from the National dial in front of the apparatus. The dial readings have no significance unless they are calibrated to units of known concentration. The dial can be read to an accuracy of approximately plus or minus 0.05 dial units using the earphones and is even more accurate using the oscilliscope.

A shift in frequency due to the fluctuation in the power supply will cause a shift in both oscillators. Since

both oscillators have a common plate and filament supply, the difference in frequency between the two oscillators is always constant and will not effect results.

To obtain a stable arrangement of 120 megacycles, the use of a 955 oscillator tube and a RG 8/U coaxial cable (90 cm.) was satisfactory. Fluctuation in the length of the cable to obtain a higher frequency results in signs of instability.

In this instrument, the relationship between change in frequency of an oscillator and capacitative-conductive effect is not known. The oscillator electrodes are curved slightly to fit around the sample container. This curvature complicates the theoretical treatment. However, the fact that this instrument has found practical application would justify its existence.

CHAPTER III

BASIS FOR CHEMICAL CALCULATIONS

According to the adherence of the results of the reactions in this study to second order kinetics, the velocity with which propionic anhydride reacts with isopropyl or n-propyl alcohols was assumed to be proportional to the concentrations of the reactants.

Starting with concentrations A (alcohol) and B (anhydride), the rate after time t, when X gram molecules of product have been formed per liter is

$$\frac{dX}{dt} = k(A-X)\ (B-X)$$

or

$$k = \frac{1}{t(A-B)} \ln \frac{B(A-X)}{A(B-X)}$$

The derivation of this expression for second order reactions is well known. In the experimental runs, the condition A = 2B was imposed. Therefore, the second order expression upon substitution is reduced to the following:

$$k = \frac{1}{t(1-0.5)} \ln \frac{0.5(1-X)}{1(0.5-X)}$$

or

$$k = \frac{1}{t(0.5)} \ln \frac{0.5(1-X)}{(0.5-X)}$$

The use of this equation in relationship to the data obtained in this study is illustrated in Chapter VI, and the

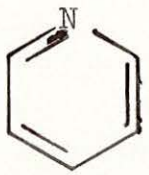
results for the rate constant of the reactions of this study listed in Tables II and IV.

Graphical treatment consists of plotting log B(A-X)/A(B-X) as ordinates versus time as abscissas. As theory requires, the plot of this data gives a straight line for second order reactions. The slope of this line multiplied by 2.303/(A-B) yields the rate constant.

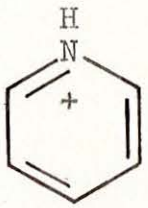
CHAPTER IV

THEORETICAL ASPECTS OF THE ESTERIFICATION

Pyridine is similar to benzene in general structure; however, due to the asymmetry of the ring, more structural isomers of pyridine are possible in comparison. The cation derived from pyridine is the pyridinium ion.



Pyridine

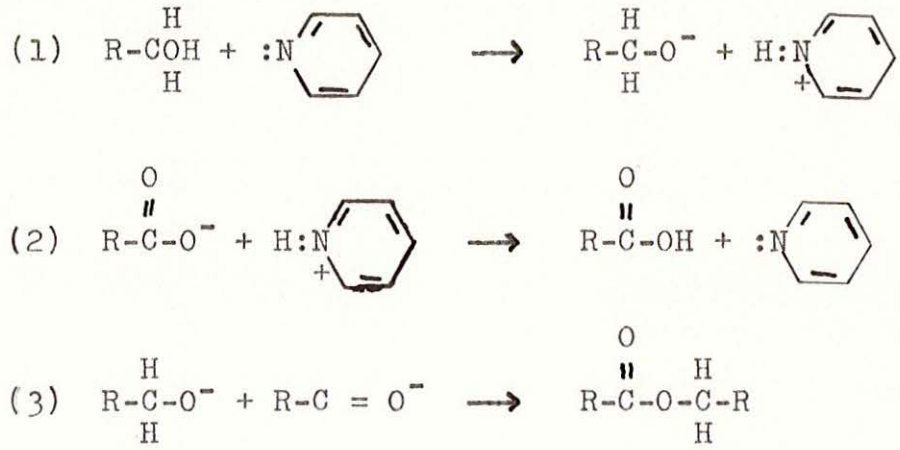


Pyridinium Ion

The resonance energy of pyridine recalculated by the method of Pauling (Cox, Challoner, and Meetham 1954) results in a value of 35 kilocalories per mole compared to the accepted value of 36 kilocalories per mole for benzene. Using the molecular arbital method (Longuet, Higgins, and Coulson 1947), it was shown that there is a considerable drift of electrons toward the nitrogen atom. As a base ($K_b = 2.3 \times 10^{-9}$), pyridine is much weaker than ammonia ($K_b = 1.8 \times 10^{-5}$). This is probably due to the changed bond hybridization of the nitrogen atom. In ammonia, the hybridization involves sp^3 orbitals, whereas in pyridine it involves sp^2 orbitals.

Using these properties of pyridine, mechanisms for

esterification reactions using pyridine as a catalyst can be proposed. In the acetylation of naphthol using pyridine as a catalyst (Conant and Bramann 1928), it was proposed that the alcohol acts as the proton donor. According to this proposal, the overall mechanism applied to the reactions in this present study could be illustrated in the following manner:

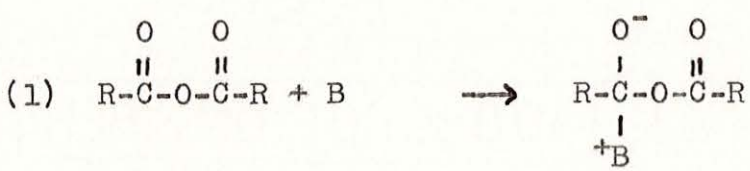


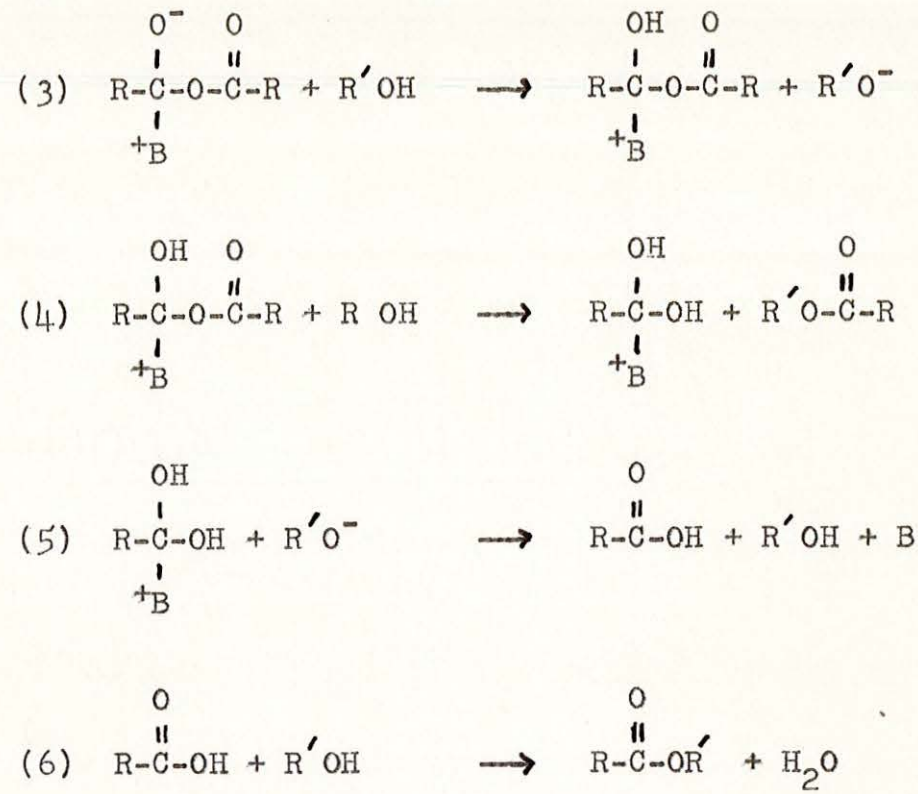
In the first step the alcohol donates a proton to a pyridine molecule resulting in the formation of a pyridinium ion and an alkoxide ion. The pyridinium ion then donates its proton to the iso or n-propionate anion--one of the products of the cleavage of the anhydride molecule--reforming the pyridine molecule and resulting in the formation of the acid. Two anions then combine to form the ester.

In non-aqueous solutions, the ionization of the acid formed is low. Therefore, if there is a possibility of the pyridine, a weak base, being neutralized by the formation of the acid, its effect on the kinetic studies should not be

serious. Another fact which must be considered is the competitive reaction involving both the acid product and the alcohol as to which would contribute its proton to the pyridine. Until the reaction reaches equilibrium, the amount of pyridinium ion formed by its reaction with the acid should be negligible. Since all the measurements were taken before equilibrium was reached, and considering the amount of alcohol present initially compared to the amount of acid before equilibrium, this competition should not seriously effect kinetic results.

In the solvolysis of acetic anhydride in methanol-water mixtures using pyridine as a catalyst (Koskikallio 1959), it was proposed that a pyridine molecule adds to the carbonyl carbon of the anhydride (Gold, Bafna, and Jefferson 1958). This mechanism can be represented by the following steps:





The addition of pyridine (B) to the carbonyl carbon of the anhydride was proposed as there is no possibility of a slow proton transfer reaction unless a solvent molecule is added to the anhydride first. The solvent molecule can then attach itself to either of two carbonyl atoms of the anhydride reaction to form the final products.

Gold, et al. (1953) showed that when B is a tertiary amine, step (1) is slow and not a reversible pre-equilibrium reaction. The products of reaction (1) should be stable because of the large separation of charge.

Both mechanisms proposed are probable. Both follow the kinetics of the reactions in this project. At present

there is no proof that either is incorrect; however, although step (2) in the first mechanism is justified, consideration of the relative basicities of the carboxylate ion and pyridine as to whether the carboxylate ion is strong enough to attract a proton from the pyridinium ion can be questioned. The carboxylate ion is stabilized by the distribution of negative charge over the two oxygen atoms in the $-COO^-$ group, whereas the pyridinium ion is also stabilized by resonance. The propionate anion should attract protons less readily than pyridine. Therefore, in this writer's opinion, the pyridinium ion should hold its proton with sufficient strength to prevent the attraction of the proton by the propionate anion.

CHAPTER V

EXPERIMENTAL PROCEDURE

I. PREPARATION OF SOLUTIONS AND REAGENTS

The materials used in this study included propionic anhydride, n-propyl and isopropyl alcohols, n-propyl and isopropyl propionates, propionic acid, and pyridine. They were prepared and purified as described in the following paragraphs.

The propionic anhydride (Eastman Distillation Products) was distilled in a 57 x 2.9 cm. vigreaux column until the fraction obtained had a boiling point range of 168-169.2 degrees centigrade. The density of this reagent was 1.010 $^{20/4}$ gms/ml.

n-Propyl alcohol (Eastman Distillation Products) was distilled in a 135 x 3 cm. helix packed column (Figure 12). The fraction used had a boiling point of 97.2-97.7 degrees centigrade, and a density of 0.8044 $^{20/4}$ gms/ml.

Isopropyl alcohol (Matheson, Coleman and Bell, Reagent ACS) was distilled in the helix packed column, and the fraction collected had a boiling point range of 81.7-82.3 degrees centigrade. The density of this reagent was 0.783-0.785 at 25 degrees centigrade.

Isopropyl propionate and n-propyl propionate both from Eastman Distillation Products were distilled in the

helix packed column. The former had a boiling point range of 110.5-111.2 degrees centigrade with a density of 0.893 gms/ml. The latter had a boiling point range of 122-123 degrees centigrade with a density of 0.883 gms/ml.

Propionic acid (Eastman Distillation Products) was distilled in the vigreaux column. The fraction retained for experimental work had a boiling point range of 140-141 degrees centigrade with a density of 0.992 gms/ml.

Pyridine (ACS Analytical Reagent) was distilled in the helix column. The fraction used had a boiling point range of 114.2-115.2 degrees centigrade with a density of 0.982 gms/ml.

After each fraction was collected, it was maintained in a glass stoppered flask, and precautions were taken to avoid contamination.

Tables I and III compare the volume of reagent used for each run to the number of moles. Each amount was delivered by means of a buret and these values were used throughout this study.

II. OPERATIONAL PROCEDURE

In order to avoid any shift in frequency or instability in the electrical components due to lack of thermal equilibrium, the oscillometer was allowed to warm up for approximately twelve hours before any measurements were made. A constant electrical source of 250 volts was maintained throughout all measurements from a Healthkit model PS-3

power supply. Due to the identical nature of the oscillators within the instrument, any fluctuation from the input voltage has the identical effect on both oscillators so the amount of electricity supplied is not critical, and the instrumental response should not vary.

To establish a relationship between dial units and concentration, the procedure consisted of filling the polyethylene sample holder with a calculated volume of reactants and products at a constant temperature. The temperature of the constant temperature bath was kept at 25 $\pm$ 0.4 degrees centigrade. The reactants and products were added first, then as soon as approximately half of the catalyst was added, the timer was started and readings were recorded. An electric stirrer was inserted to insure homogeniety. To cover the sample holder, a cork, through which a hole was drilled for the stirrer, was used. This minimized the loss of volatile components through vaporization.

A series of timed readings were recorded graphically and the value at zero time was obtained by extrapolation. By this method, a graph could be constructed relating the dial reading directly to the concentration of propionic anhydride. From this graph, a relationship between the concentration of propionic anhydride to time can be obtained. In this way, measurement of the disappearance of one of the reactants can be achieved, and ultimately the rate constant

for the reaction calculated.

A zero or standard solution was not employed in this investigation because each run was reproduced to plus or minus one to two dial units. The duplicated runs for each reaction were usually completed on the same day to avoid fluctuations in the instrument due to weather or temperature changes.

CHAPTER VI

CALCULATIONS AND RESULTS

The rate constants in Tables II and IV were calculated on the theoretical interpretation of the kinetics of Chapter III. The initial concentration of the reactants was 0.5 moles of propionic anhydride and 1.0 moles of alcohol. The initial concentration was used in all experimental runs. The reaction variable X was determined directly from the plot of moles of propionic anhydride (B-X) versus time.

Using two milliliters of pyridine as a catalyst, a typical calculation to obtain the rate constant for the reaction between isopropyl alcohol and propionic anhydride can be illustrated. At t = 13,000 seconds, (B-X) is equal to 0.4 moles of propionic anhydride and (A-X) is equal to 0.9 moles of isopropyl alcohol. These values can then be substituted into the following expression:

$$k = \frac{2.3}{t(A-B)} \cdot \log \frac{B(A-X)}{A(B-X)}$$

$$k = \frac{2.303}{13,000(0.5)} \cdot \log \frac{(0.5)(0.9)}{(1)(0.4)} \cdot 0.1428 \text{ liters}$$

$$k = 2.588 \times 10^{-6} \text{ liters seconds}^{-1} \text{ moles}^{-1}$$

The volume of reactants was taken as 0.1428 liters in all instances with the isopropyl alcohol and propionic anhydride reaction, and 0.1417 liters with the n-propyl alcohol and propionic anhydride reaction.

The rate constants were also determined from the slope of the line from the plot of log B(A-X)/A(B-X) versus time. The product is then multiplied by the volume.

For a typical calculation, consider the results of Figure 8. In this case, the slope of the line is equal to 0.01428. The calculation for the rate constant would be as follows:

$$k = \frac{(2.303)(0.01428)}{(A-B)} \cdot (0.1417 \text{ liters})$$

$$= 0.9324 \times 10^{-4} \text{ liters seconds}^{-1} \text{ moles}^{-1}$$

By use of the resonance method of a wavelength of 150 m., Akerlöf (1932) found that the dielectric constants of isopropyl and n-propyl alcohols varied at 20 degrees centigrade according to percentage water in the alcohol.

Alcohol (Weight %)	Dielectric Constant n-propyl alcohol	Dielectric Constant isopropyl alcohol
0	80.37	80.37
10	73.52	73.11
20	66.54	65.72

Alcohol (Weight %)	Dielectric Constant n-propyl alcohol	Dielectric Constant isopropyl alcohol
30	59.21	58.40
40	51.68	51.07
50	44.29	43.68
60	37.51	36.28
70	31.56	29.57
80	26.83	24.44
90	23.34	20.95
100	20.81	18.62

It is known that both esters formed as products of the esterification are soluble up to 0.5-0.6 grams per 100 milliliters of water. Therefore, if the reaction is of an order where the formation of water forms a heterogeneous mixture in the period at which measurements are taken, kinetic results can be unfavorable using the high frequency oscillometer. The rate constant for the n-propyl alcohol-propionic anhydride reaction was on the order of 1×10^{-2} liters $second^{-1}$ $mole^{-1}$, whereas for the isopropyl alcohol-propionic anhydride reaction the rate constant was on the order of 3×10^{-6} liters $seconds^{-1}$ $mole^{-1}$. From Figure 8, the results in the rate constant are not scattered as in Figure 4. The rate constant is increasing with time in Figure 8. This might suggest a change in order of the reaction after a period of time. However, in this writer's

opinion, the results of the reaction involving the formation of n-propyl propionate could not be reliable due to the formation of a heterogeneous mixture.

It should be pointed out that the total volume used in the calculations of both reactions is only approximate. Therefore, the significance of the reactions should be the difference in the order of the rate constants.

CHAPTER VII

SUMMARY

The base catalyzed esterification of propionic anhydride with n-propyl and isopropyl alcohols were investigated using a one hundred and twenty megacycle oscillometer with the purpose of determining the velocity of the reaction.

The possible complications that may effect the kinetic results were discussed as well as the resulting heterogeneous mixture in one of the reactions. The instrument is, in the writer's opinion, satisfactory for polynary solutions as long as there is a difference in the capacitative effects of the reactants and products. However, the results obtained from the formation of heterogeneous mixtures could not be reliable.

It might also be mentioned that the absence of a mathematical interpretation relating instrumental response to dielectric change should be a limiting factor in the use of the high frequency oscillometer, used in this study, as an analytical tool.

The method used in this investigation was not an original one, but adapted from a previous investigation (Lowery 1958) which involved the study of a similar reaction using a high frequency oscillometer operating in the 120 megacycle range to measure the changing electrical properties of a reaction, and ultimately relating these changes to the

rate constant for the particular reaction.

TABLE I

COMPARISON OF VOLUME (ML.) TO MOLES OF REAGENT

PROPIONIC ANHYDRIDE		ISOPROPYL ALCOHOL		ISOPROPYL PROPIONATE		PROPIONIC ACID	
VOLUME	MOLES	VOLUME	MOLES	VOLUME	MOLES	VOLUME	MOLES
65.43	0.5	76.56	1.0	0	0	0	0
51.54	0.4	69.90	0.9	13.01	0.1	7.47	0.1
25.77	0.2	53.59	0.7	39.02	0.3	22.40	0.3
0.0	0	38.28	0.5	65.03	0.5	37.34	0.5

TABLE II

EXPERIMENTAL DATA FOR THE REACTION BETWEEN ISOPROPYL ALCOHOL AND PROPIONIC ANHYDRIDE AT 25 DEGREES CENTIGRADE (2 ML. PYRIDINE)

TIME (SEC.)	(B-X)	(A-X)	$\log\frac{B(A-X)}{A(B-X)}$	k(LITERS MOLE^{-1} SEC^{-1})
13,000	.4	.9	0.05115	2.588×10^{-6}
27,000	.3	.8	0.12483	3.040×10^{-6}
55,000	.2	.7	0.24304	2.906×10^{-6}

$$\text{SLOPE OF LINE} = \frac{k(A-B)}{2.303} = \frac{.1}{2.2 \times 10^{4}}$$

$$k = (2.303)\ \frac{1}{22 \times 10^{4}}\ (A-B) \times .1428 \text{ LITERS}$$

$$= 2.9897 \times 10^{-6} \text{ LITERS MOLE}^{-1}\text{SEC}^{-1}$$

B = PROPIONIC ANHYDRIDE

A = ISOPROPYL ALCOHOL

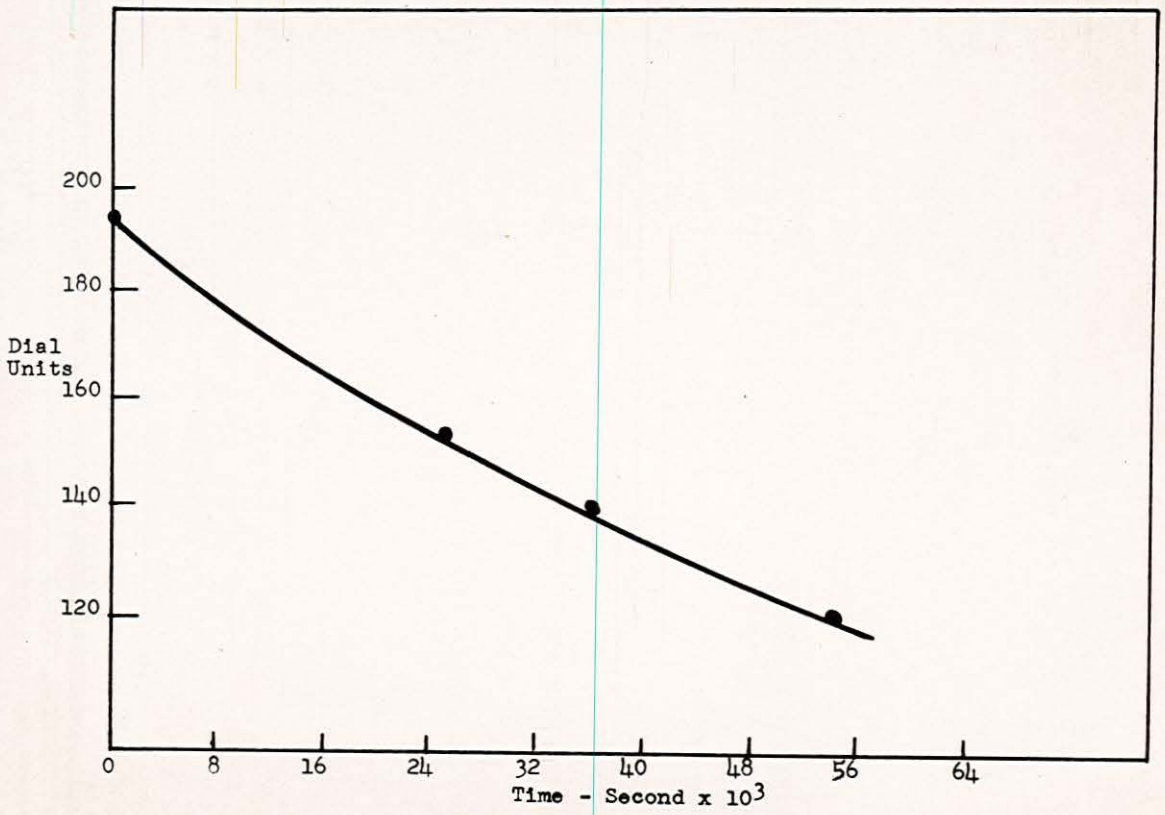


FIGURE 1

INSTRUMENTAL RESPONSE TO THE REACTION BETWEEN
ISOPROPYL ALCOHOL WITH PROPIONIC ANHYDRIDE
AT 25 DEGREES CENTIGRADE

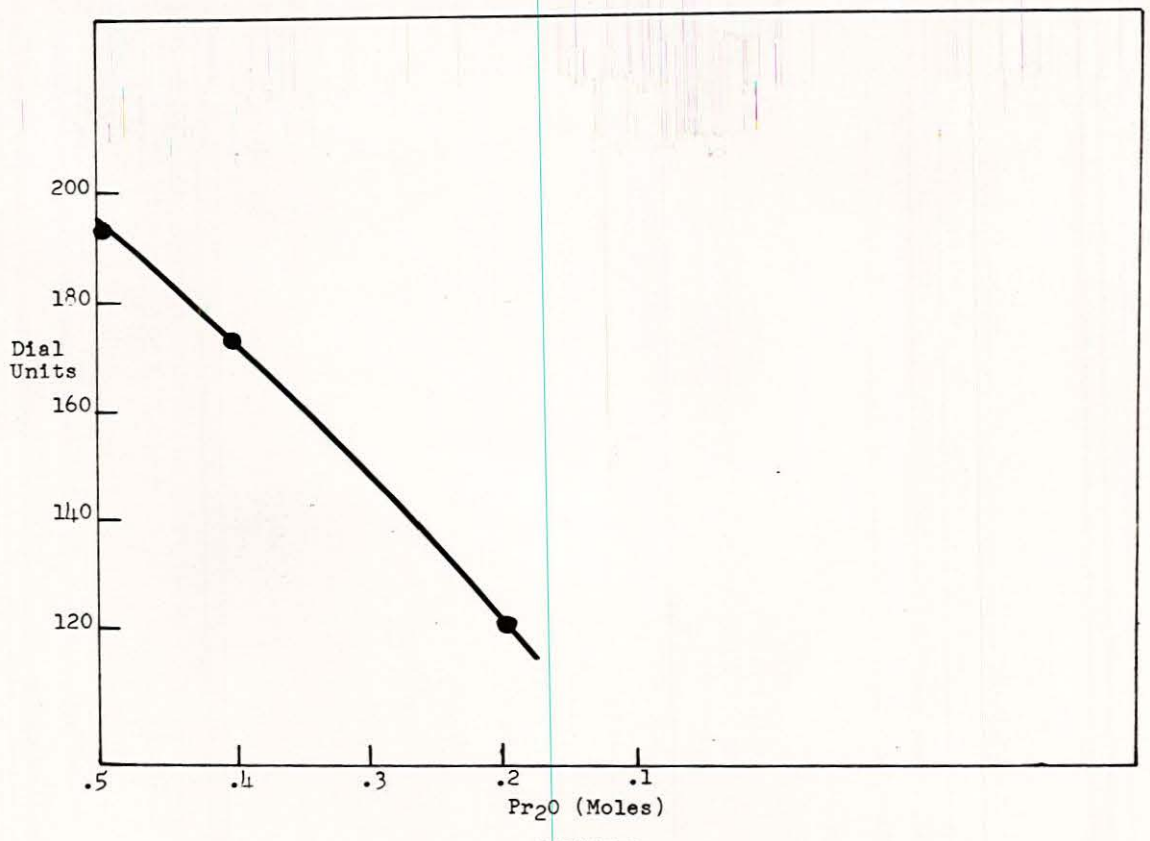


FIGURE 2

CHANGE IN DIAL UNITS WITH RESPECT TO
CONCENTRATION OF PROPIONIC ANHYDRIDE

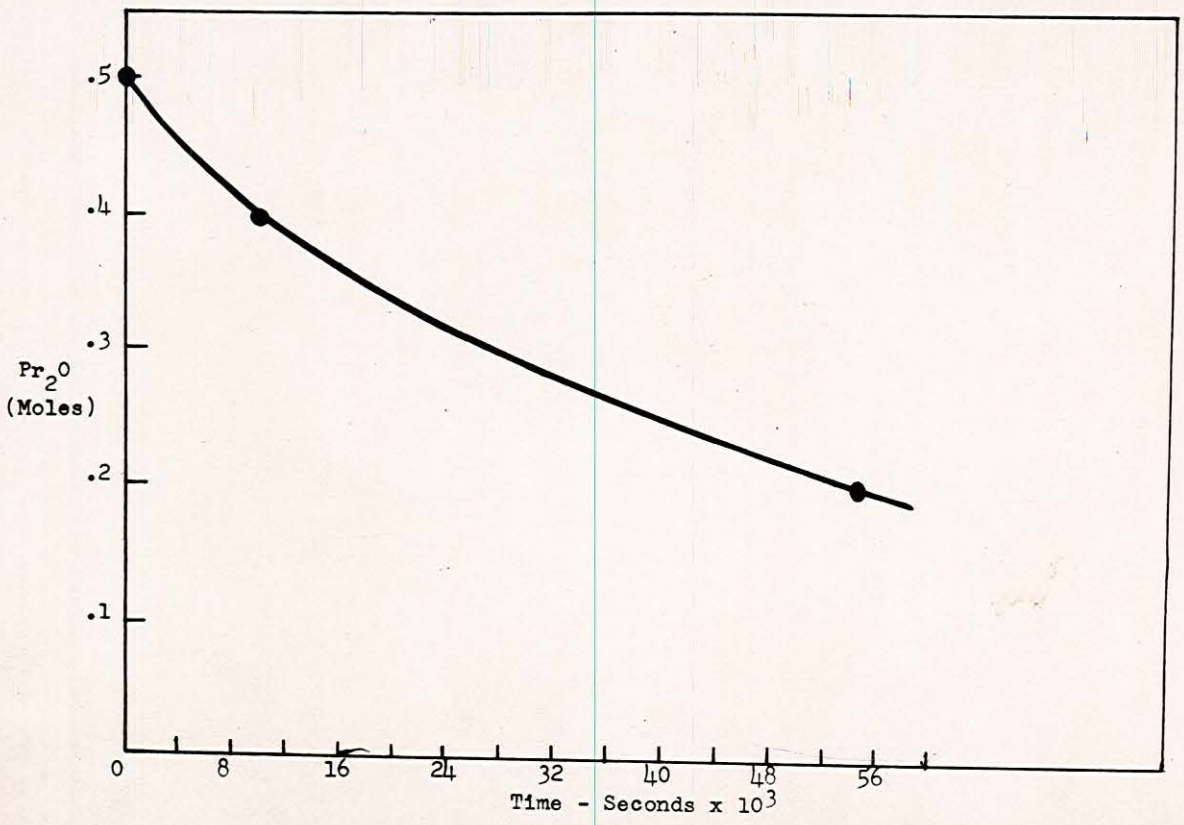


FIGURE 3

CHANGE IN CONCENTRATION OF PROPIONIC ANHYDRIDE WITH RESPECT TO TIME

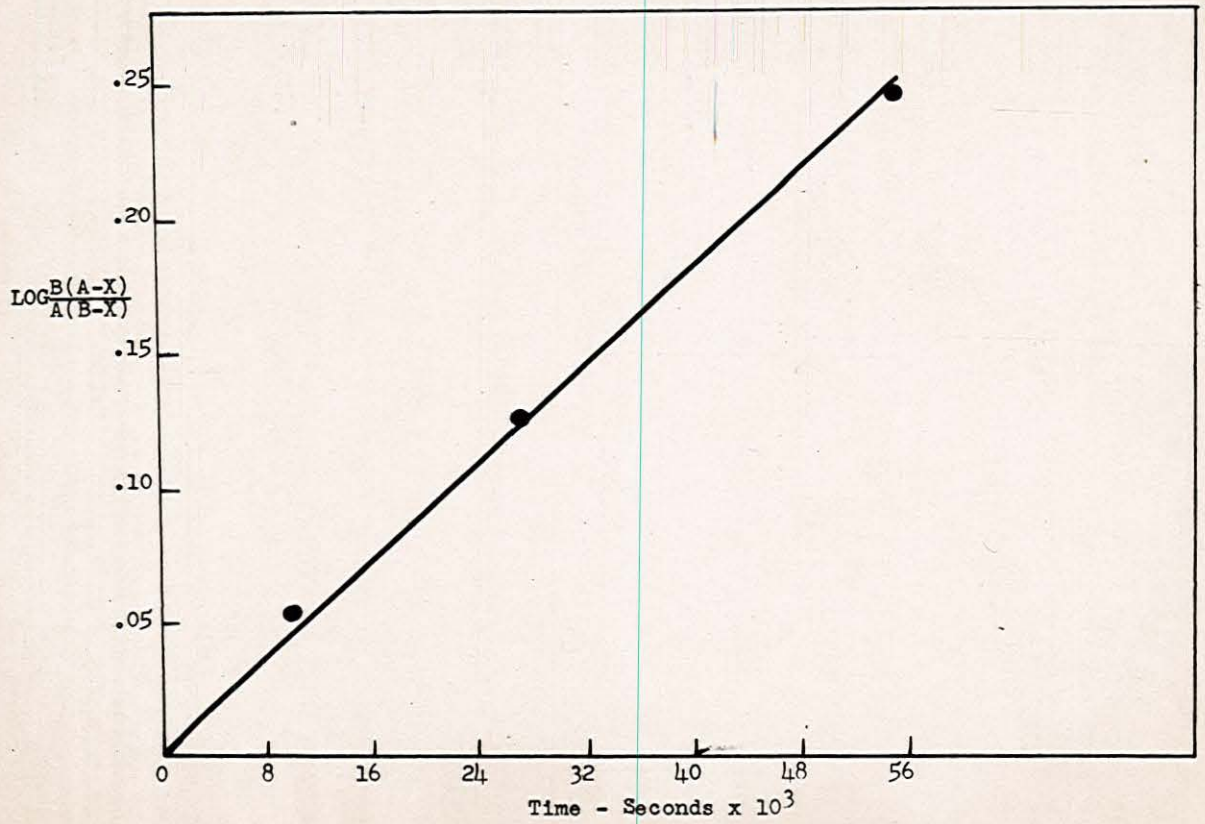


FIGURE 4

LOG-B(A-X)/A(B-X) VERSUS TIME

TABLE III

COMPARISON OF VOLUME (ML.) TO MOLES OF REAGENT

PROPIONIC ANHYDRIDE		n-PROPYL ALCOHOL		n-PROPYL PROPIONATE		PROPIONIC ACID	
VOLUME-	MOLES	VOLUME-	MOLES	VOLUME-	MOLES	VOLUME-	MOLES
65.43	0.5	74.71	1.0	0	0	0	0
51.54	0.4	67.24	0.9	13.16	0.1	7.47	0.1
25.77	0.2	52.37	0.7	39.47	0.3	22.40	0.3
0.0	0	37.36	0.5	65.77	0.5	37.34	0.5

TABLE IV

EXPERIMENTAL DATA FOR THE REACTION BETWEEN
n-PROPYL ALCOHOL AND PROPIONIC ANHYDRIDE
AT 25 DEGREES CENTIGRADE (2 ML. PYRIDINE)

TIME (SEC.)	(B-X)	(A-X)	$\text{LOG}\frac{B(A-X)}{A(B-X)}$	k(LITERS MOLE^{-1} SEC^{-1})
3.55	.4	.9	0.05115	0.9538×10^{-2}
8.5	.3	.8	0.1248	0.9583×10^{-2}
15.0	.2	.7	0.2430	1.0573×10^{-2}

SLOPE OF LINE = $\frac{k(A-B)}{2.303} = \frac{.1}{7}$

$k = 2.303 \frac{.1}{7} \quad (A-B) \times .1417$ LITERS

$= .9324 \times 10^{-2}$ LITERS MOLE^{-1}SEC^{-1}

B = PROPIONIC ANHYDRIDE

A = n-PROPYL ALCOHOL

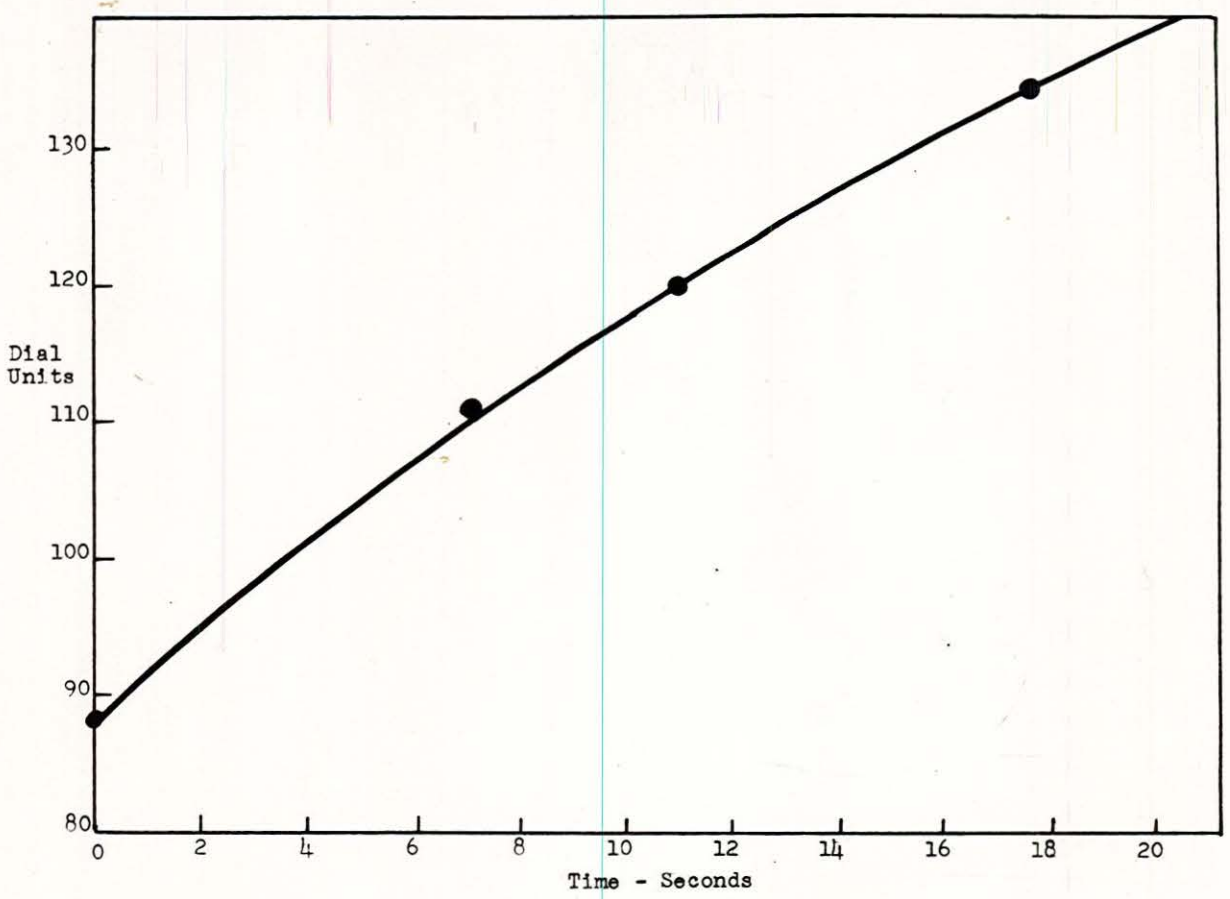


FIGURE 5

INSTRUMENTAL RESPONSE TO THE REACTION BETWEEN
n-PROPYL ALCOHOL WITH PROPIONIC ANHYDRIDE
AT 25 DEGREES CENTIGRADE

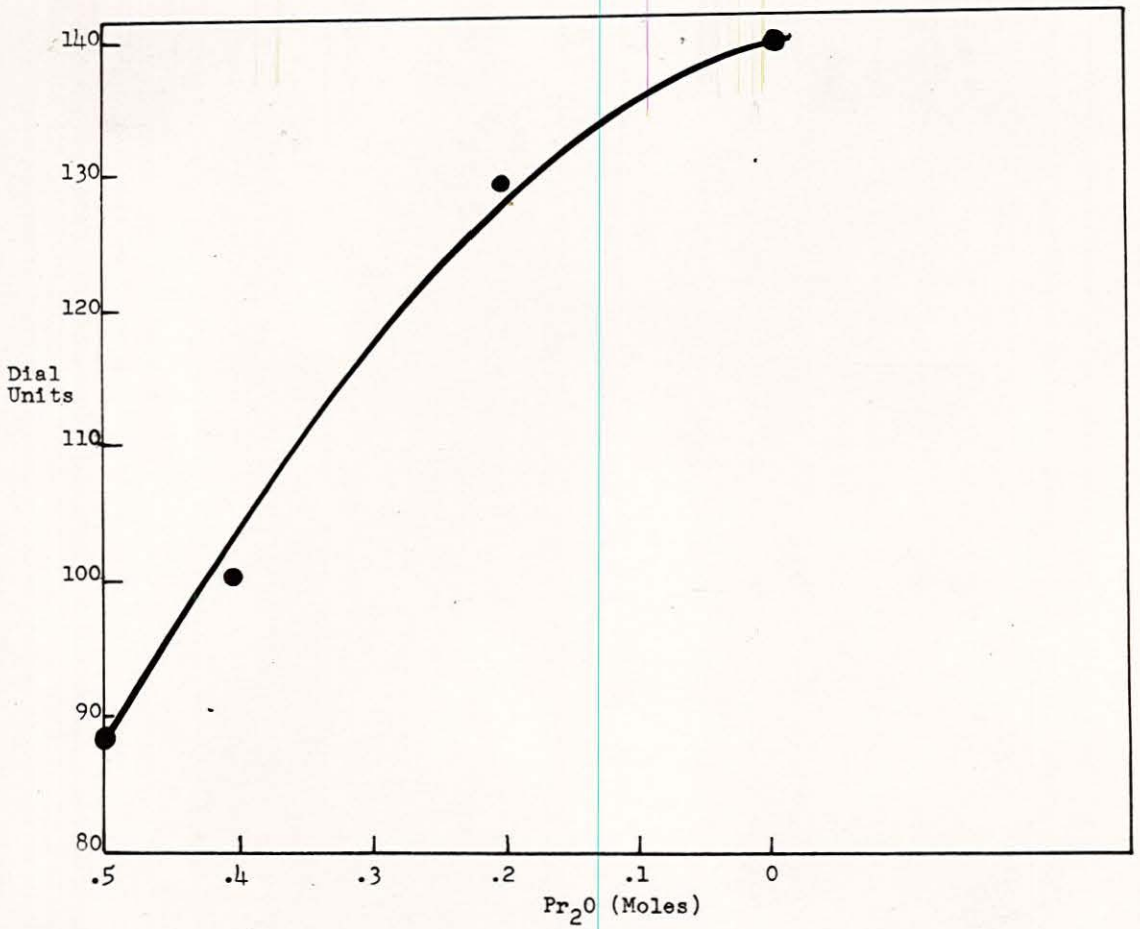


FIGURE 6

CHANGE IN DIAL UNITS WITH RESPECT TO
CONCENTRATION OF PROPIONIC ANHYDRIDE

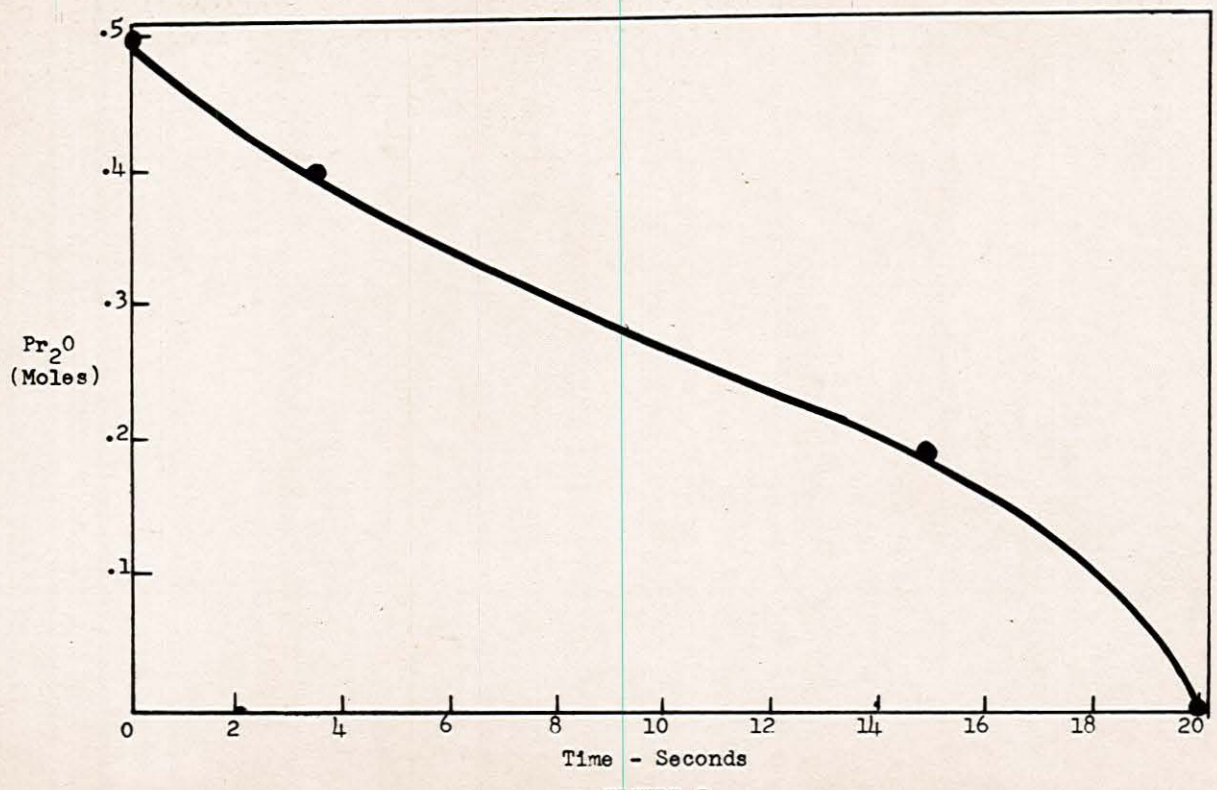


FIGURE 7

CHANGE IN CONCENTRATION OF PROPIONIC ANHYDRIDE WITH RESPECT TO TIME

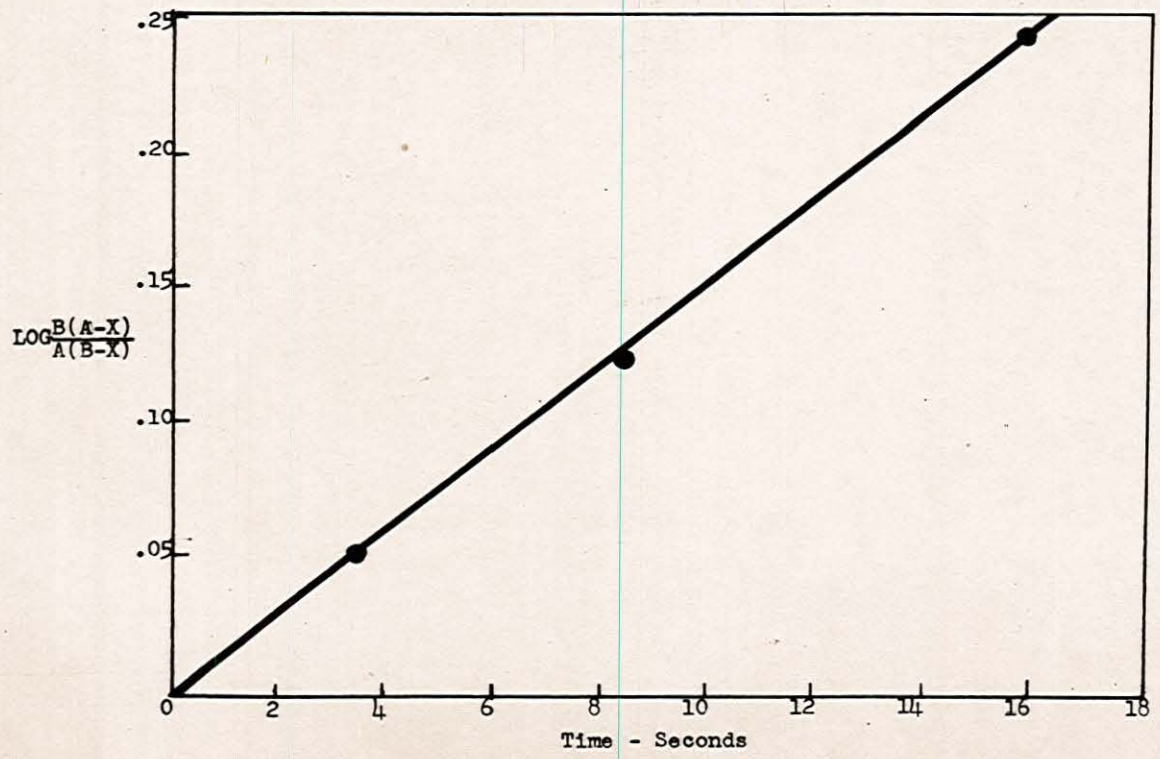


FIGURE 8

LOG B(A-X)/A(B-X) VERSUS TIME

FIGURE 9

INSTRUMENT, POWER SUPPLY, OSCILLOSCOPE, AND TIMER

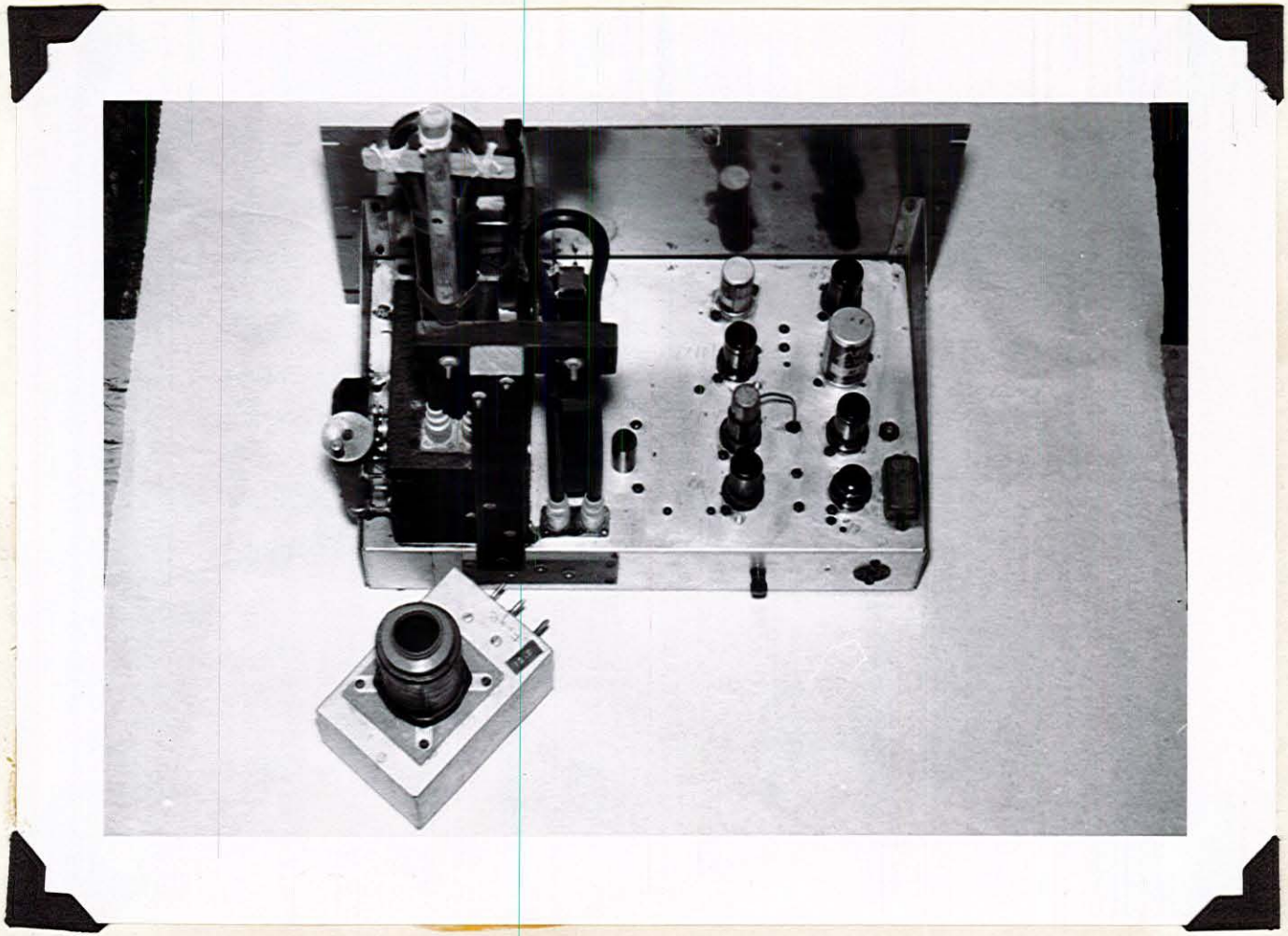


FIGURE 10

INSTRUMENT - BACK VIEW

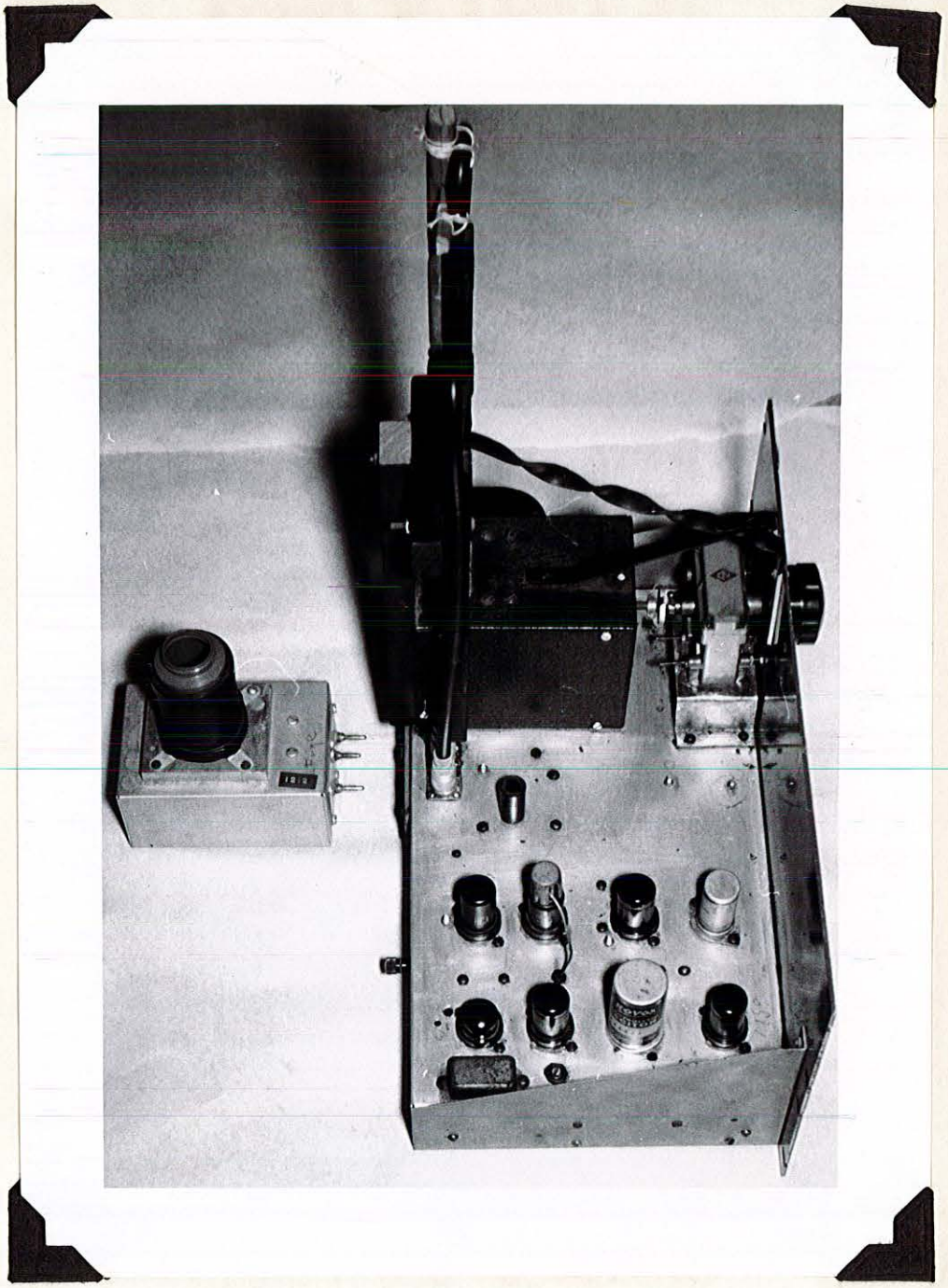


FIGURE 11

INSTRUMENT - SIDE VIEW

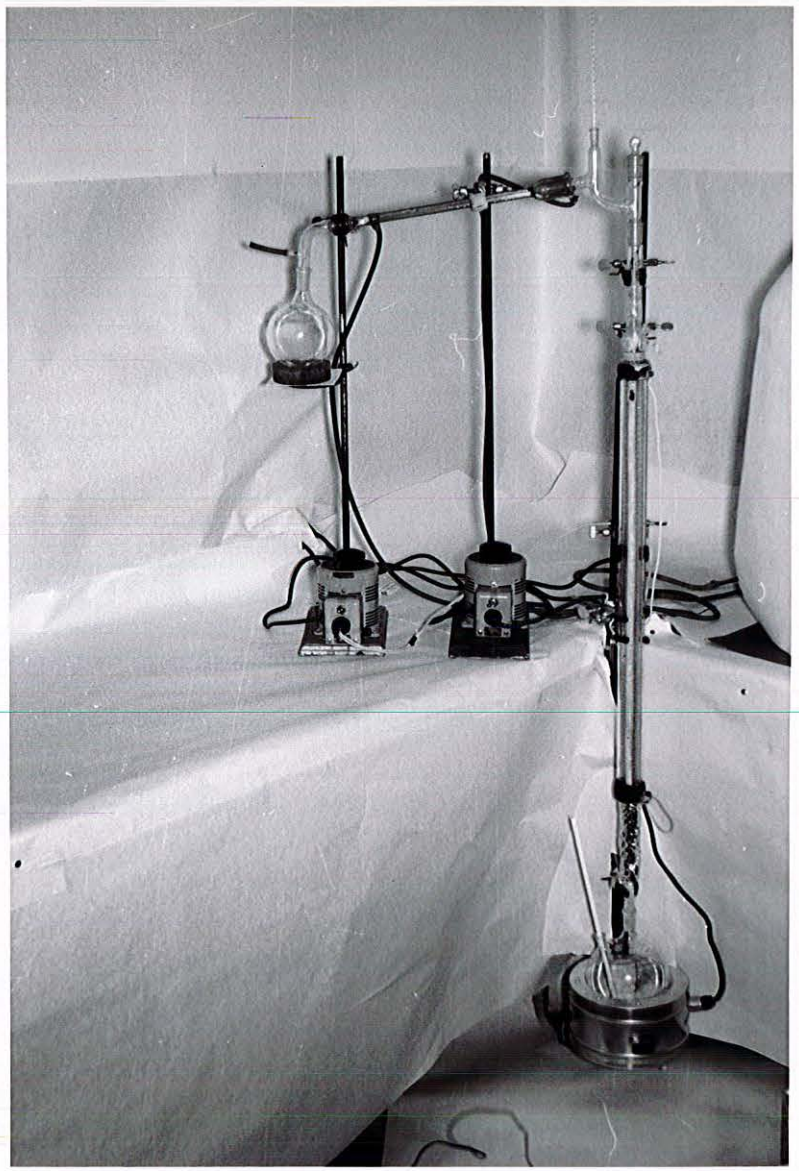


FIGURE 12

DISTILLATION APPARATUS

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